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MEMORANDUM FOR PRR (Contractor Publication)

10 February 1999

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K.O. Christe, D.A. Dixon et al. (RSTX) and J.A. Sheehy, "A Quantitative Scale for the Strength of Lewis Acids" and "On the Reaction of N_2F^+ with HN_3 and the Synthesis and Characterization of $N_5^+AsF_6^-$"

(Statement A)

Presentation

A QUANTITATIVE SCALE FOR THE STRENGTH OF LEWIS ACIDS

KARL O. CHRISTE, DAVID A. DIXON, DOUGLAS McLEMORE

ON THE REACTION OF N_2F^+ WITH HN_3 AND THE SYNTHESIS AND CHARACTERIZATION OF $N_5^+AsF_6^-$

KARL O. CHRISTE, WILLIAM W. WILSON, JEFFREY A. SHEEHY

QUANTITATIVE SCALE FOR THE STRENGTH OF LEWIS ACIDS

TWO TYPES OF ACIDS

- BRONSTED OR PROTIC ACIDS (PROTON DONORS)

$$HA + H_20 \rightleftarrows H_3O^+_{(solv)} + A^-_{(solv)}$$

QUANTITATIVE SCALES ARE KNOWN : pH AND pK SCALES

IONIC PRODUCT OF H_2O

$$K_w = [H_3O^+][OH^-] = 10^{-14} \qquad pH = -\log [H_3O^+]$$

$$pK_\alpha = -\log K_\alpha = [H^+][A^-]/[HA]$$

- LEWIS ACIDS (ELECTRON ACCEPTORS)

DONOR $\longrightarrow$ ACCEPTOR INTERACTION

(LEWIS BASE) (LEWIS ACID)

STRENGTH IS DIFFICULT TO MEASURE

NO QUANTITATIVE SCALE KNOWN

PROPOSED LEWIS ACID STRENGTH SCALE

- F^- ION IS A VERY STRONG LEWIS BASE

  HAS A SMALL DIAMETER

  INTERACTS WITH MOST LEWIS ACIDS

  IS WELL SUITED FOR THEORETICAL CALCULATIONS

- F^- AFFINITY (FA) INCREASES WITH LEWIS ACID STRENGTH AND, THEREFORE, CAN SERVE AS A BASIS FOR A QUANTITATIVE LEWIS ACIDITY SCALE

- ONLY FEW F^- AFFINITY DATA WERE AVAILABLE ESPECIALLY FOR INORGANICS;

  MANY WERE ONLY QUALITATIVE (CYCLOTRON RESONANCE BRACKETING AND EQUILIBRIUM MEASUREMENTS)

  LARGE ERRORS AND DIFFERENT METHODS GAVE DIFFERENT RESULTS

- NEEDED

  A QUANTITATIVE, INTERNALLY CONSISTENT SET OF FA'S FOR ANY DESIRED LEWIS ACID

METHODS FOR CONSTRUCTION OF QUANTITATIVE F^- AFFINITY SCALE

- THEORETICAL CALCULATIONS, USING POLARIZED DOUBLE-ZETA BASIS SETS, WERE PERFORMED AT THE FOLLOWING LEVELS

  LDF

  NLDF

  MP2

- TO SIMPLIFY THE CALCULATIONS, BECAUSE THE ELECTRON AFFINITY OF F IS HARD TO CALCULATE, COF_2 WAS USED AS A REFERENCE COMPOUND

$$F_3CO^- + B \longrightarrow COF_2 + BF^-$$

- TO CONVERT TO ABSOLUTE VALUES, THE EXPERIMENTALLY KNOWN FA OF COF_2 (49.9 kcal/mol) WAS ADDED TO THE RELATIVE FA VALUES

PROPOSAL OF A pF SCALE FOR LEWIS ACIDITY

- F^- AFFINITIES WERE CALCULATED FOR 106 LEWIS ACIDS AND RANGE FROM 0 - 120 kcal/mol ON THE ABSOLUTE SCALE GIVING A VALUE OF FA (AlF_3) = 115 kcal/mol, THE SAME AS DETERMINED BY THERMODYNAMIC EXPERIMENT

- TO OBTAIN A LEWIS ACIDITY SCALE RANGE COMPARABLE TO THE FAMILIAR pH SCALE RANGE OF 0-14, THE FOLLOWING CONVENTION IS PROPOSED

$$\boxed{pF = \frac{F^- \text{ AFFINITY (kcal/mol)}}{10}}$$

GIVING A pF RANGE OF 0-12,WITH 12 BEING THE VALUE FOR THE STRONGEST KNOWN LEWIS ACID (SbF_5)

ABBREVIATED pF SCALE

(CHRISTE, DIXON, McLEMORE)

COMPOUND	pF	COMPOUND	pF	COMPOUND	pF
SbF_5	12.03	cis-IO_2F_3	9.66	SOF_4	6.60
AlF_3	11.50	PF_5	9.49	$XeOF_4$	6.37
$AlFCl_2$	11.50	$SeOF_4$	8.69	TeF_6	6.15
AlF_2Cl	11.47	TeF_4	8.34	POF_3	5.86
$AlCl_3$	11.46	BF_3	8.31	XeF_4	5.71
$TeOF_4$	10.79	GeF_4	8.30	SF_4	5.67
InF_3	10.75	ClF_5	7.47	COF_2	4.99
GaF_3	10.70	BrF_3	7.35	PF_3	4.49
AsF_5	10.59	SiF_4	7.35	HF	3.68
SnF_4	9.82	SeF_4	7.12	NO_2F	1.92
				NOF	1.74

SPECIAL COMMENTS ABOUT THE pF SCALE

- pF VALUES ARE FOR THE FREE ISOLATED MOLECULES
- VALUES FOR ASSOCIATED SOLIDS MUST BE CORRECTED
- FORMATION OF COMPLEX FLUORO ANIONS CAN BE CORRELATED WITH THE pF SCALE AND BECOMES DIFFICULT BELOW pF $\sim$ 3.5
- PREPRINTS OF PAPER SHOULD BECOME AVAILABLE WITHIN 4-8 WEEKS

N_2F^+ CHEMISTRY AND SYNTHESIS OF $N_5^+AsF_6^-$

- HOMOLEPTIC POLYNITROGEN COMPOUNDS ARE OF GREAT INTEREST FOR HIGH ENERGY DENSITY MATERALS (HEDM)

- MANY THEORETICAL STUDIES DURING THE PAST 15 YEARS HAVE BEEN DONE, BUT NO SUCCESSFUL SYNTHESIS OF A HOMOLEPTIC POLYNITROGEN HEDM HAS BEEN REPORTED

- ONLY TWO HOMOLEPTIC POLYNITROGEN COMPOUNDS ARE KNOWN WHICH CAN BE PREPARED IN SUBSTANCE

N_2	1772	RUTHERFORD, SCHEELE, CAVENDISH
N_3^-	1890	CURTIUS

PROBLEMS WITH SYNTHESIS OF POLYNITROGEN HEDM

- ALL THE ENERGY MUST COME FROM ENDOTHERMICITY WHICH MAKES POLYNITROGEN HEDM EXTREMELY DANGEROUS

  (SENSITIVITY INCREASES WITH INCREASING ENERGY)

- BASIS FOR HIGH ENERGY CONTENT ARE THE LARGE DIFFERENCES IN BOND ENERGIES FOR N-N BONDS

N-N	38 kcal/mol	C-C	85 kcal/mol
N=N	100 kcal/mol	C=C	143 kcal/mol
N≡N	228 kcal/mol	C≡C	194 kcal/mol

$$\underset{38 + 100}{-(N{=}N)_n-} \xrightarrow{-90} \underset{228}{|N{\equiv}N|}$$

$$\underset{85 + 143}{-(CH{=}CH)_n-} \xrightarrow{+34} \underset{194}{CH{\equiv}CH}$$

EXCEPTIONS: N_2, O_2

STABLE MONOMERS
UNSTABLE POLYMERS

NORMAL CASE:

STABLE POLYMERS
UNSTABLE MONOMERS

GENERAL CONCEPT FOR POLYNITROGEN HEDM SYNTHESIS

- ALL POLYNITROGEN COMPOUNDS ARE UNSTABLE WITH RESPECT TO N_2

- ACTIVATION ENERGY BARRIER TOWARD N_2 ELIMINATION IS DETERMINED BY THE WEAKEST BOND IN POLYNITROGEN COMPOUND

- THE BARRIER AND METASTABILITY OF POLYNITROGEN COMPOUNDS MUST BE INCREASED BY SUITABLE RESONANCE STRUCTURES

$$[\,|N-N\equiv N|\,]^- \longleftrightarrow [\,\langle N=N=N\rangle\,]^- \longleftrightarrow [\,|N\equiv N-N|\,]^-$$

- DOUBLE BOND CHACTER OF N-N BONDS IN AZIDE ION EXPLAINS ITS EXCEPTIONAL STABILITY

- HOW CAN THIS STABILIZATION EFFECT BE TAKEN ADVANTAGE OF?

EXPANSION OF THE AZIDE STRUCTURE

- ADDITION OF $[N]^+$ UNITS TO N_3^-

$$[N{=}N{=}N]^- + [N]^+ \longrightarrow \underset{N_4}{N{=}N{=}N{=}N}$$

$$N{=}N{=}N{=}N + [N]^+ \longrightarrow \underset{N_5^+}{[N{=}N{=}N{=}N{=}N]^+}$$

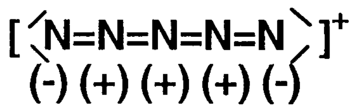
- HOWEVER, THEORETICAL CALCULATIONS SHOW THAT $D_{\infty h}$ N_4 IS NOT STABLE

$$\underset{(-)\,(+)\,(+)\,(-)}{N{=}N{=}N{=}N}$$ <u>NEIGHBORING CHARGES OF EQUAL SIGN MUST BE AVOIDED</u>

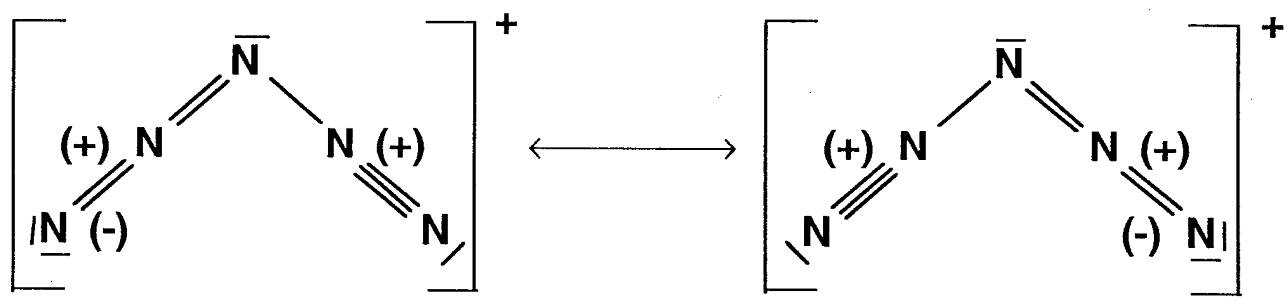
- NO PLAUSIBLE RESONANCE STRUCTURES CAN BE WRITTEN FOR N_4 WHICH RETAIN DOUBLE BOND CHARACTER WHILE AVOIDING NEIGHBORING CHARGES OF EQUAL SIGN

EXPANSION OF THE AZIDE STRUCTURE TO N_5^+

- THE SAME PROBLEM EXISTS FOR N_5^+ WITH NEIGHBORING POSITIVE CHARGES



- RESONANCE STRUCTURES, HOWEVER, CAN BE WRITTEN WHICH AVOID THIS PROBLEM



- AB INITIO CALCULATIONS (CCSD(T) AND B3LYP) CONFIRM THE STABILITY OF THIS C_{2v} STRUCTURE

SELECTION OF SUITABLE STARTING MATERIALS FOR N_5^+ SYNTHESIS

- REQUIREMENTS

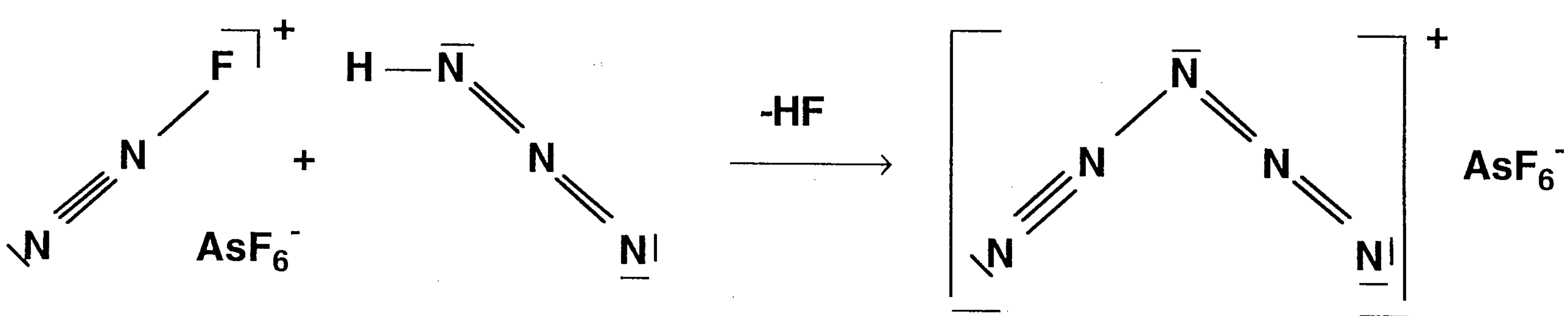
  STARTING FRAGMENTS MUST HAVE ALREADY BUILT IN WEAKENED BONDS

  MUST HAVE A FORMAL POSITIVE CHARGE (IP OF N_2 = 359 kcal/mol)

  COUPLING REACTION MUST BE EXOTHERMIC

  CHOICE OF SUITABLE SOLVENT (HEAT SINK, STABILIZATION, SAFETY)

- IDEAL CANDIDATE SYSTEM



ACTUAL SYNTHESIS OF $N_5^+AsF_6^-$

- SYSTEM WORKED AS PLANNED

  $$N_2F^+AsF_6^- + HN_3 \xrightarrow[-78^\circ C]{HF} N_5^+AsF_6^- + HF$$

  HIGH YIELD

  ONLY OTHER BYPRODUCT 20-40% $H_2N_3^+AsF_6^-$

  2 MMOL (0.5 G SCALE)

- PROPERTIES OF $N_5^+AsF_6^-$

  WHITE SOLID

  SPARINGLY SOLUBLE IN HF

  MARGINALLY STABLE AT 22 °C

  HIGHLY ENERGETIC

  REACTS VIOLENTLY WITH WATER AND ORGANICS

  CALCULATED $\Delta H_f^\circ\ N_5^+{}_{(g)}$ = 353 kcal/mol

SYNTHESIS OF ^{15}N LABELED $N_5^+AsF_6^-$

$$2\,NaN^*NN + 2\,CH_3(CH_2)_{16}CO_2H \xrightarrow{80^\circ C} HN^*NN + HNNN^* + 2\,NaO_2C(CH_2)_{16}CH_3$$

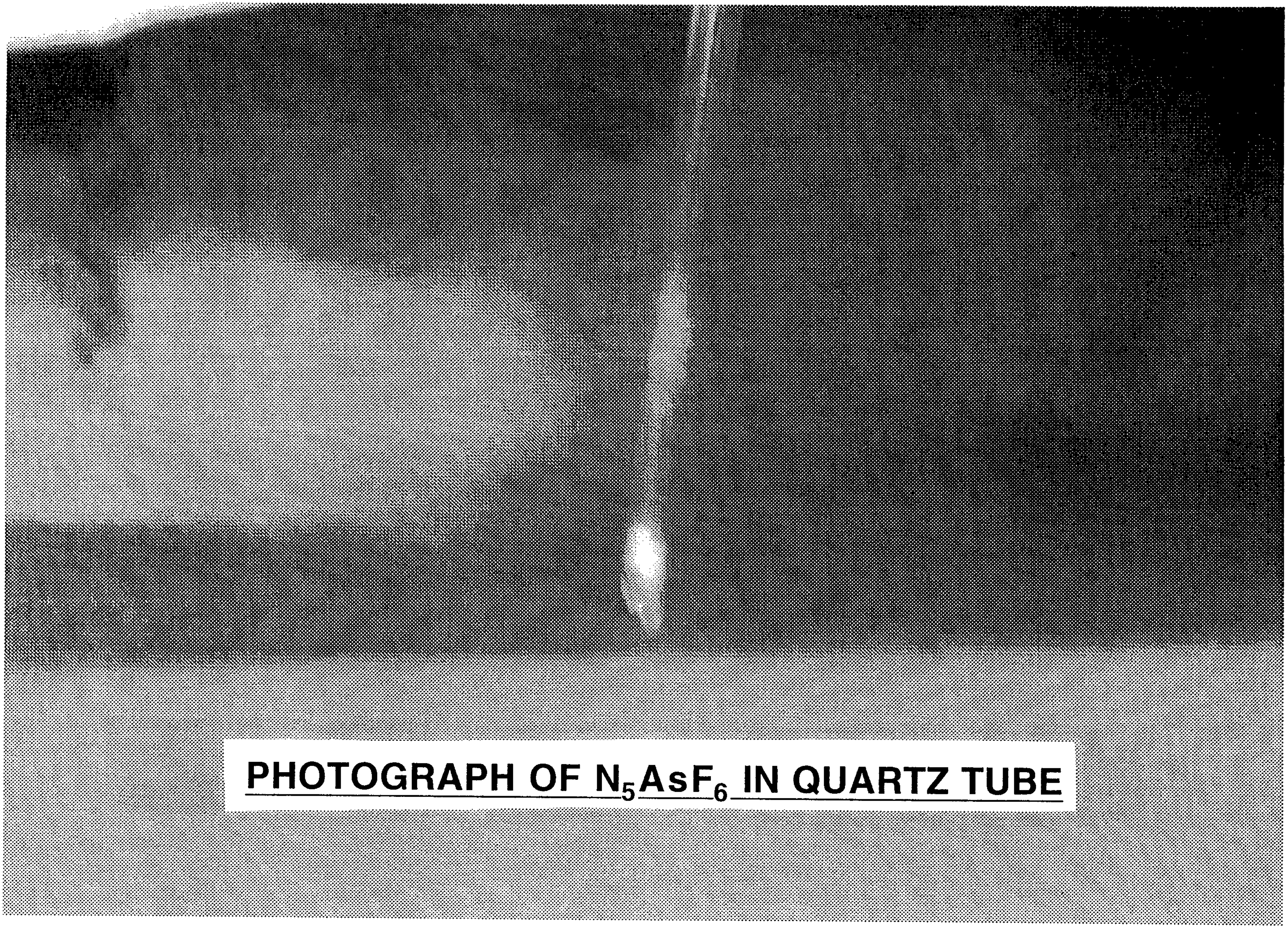
$$2\,N_2F^+AsF_6^- + HN^*NN + HNNN^* \longrightarrow [N^*NNNN]^+AsF_6^- + [NNN^*NN]^+AsF_6^- + 2\,HF$$

^{15}N LABELED N_5AsF_6 NEEDED FOR POSITIVE IDENTIFICATION OF N_5^+ BY SPECTROSCOPIC METHODS

CHARACTERIZATION OF $N_5^+AsF_6^-$

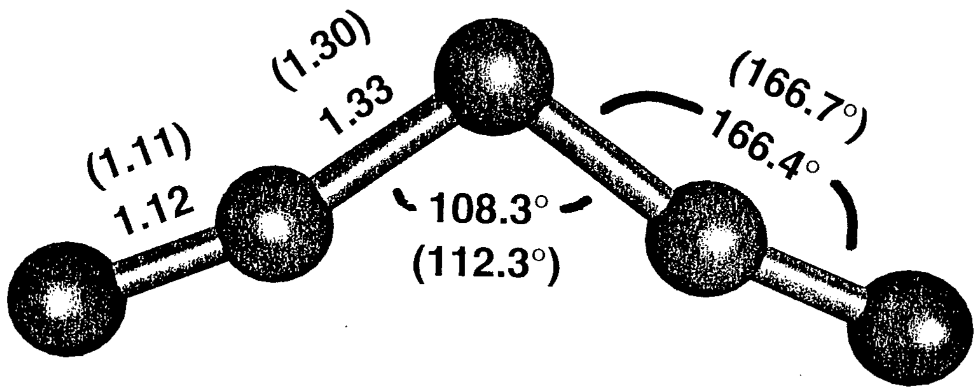
- ^{14}N AND ^{15}N NMR SPECTRA
- LOW-TEMPERATURE RAMAN AND INFRARED SPECTRA OF NORMAL AND ISOTOPICALLY LABELED N_5^+
- NORMAL COORDINATE ANALYSIS
- MASS SPECTROSCOPY
- THEORETICAL CALCULATIONS

  OPTIMIZED GEOMETRY
  VIBRATIONAL SPECTRA
  ISOTOPIC SHIFTS
  NMR SHIFTS
  HEAT OF FORMATION



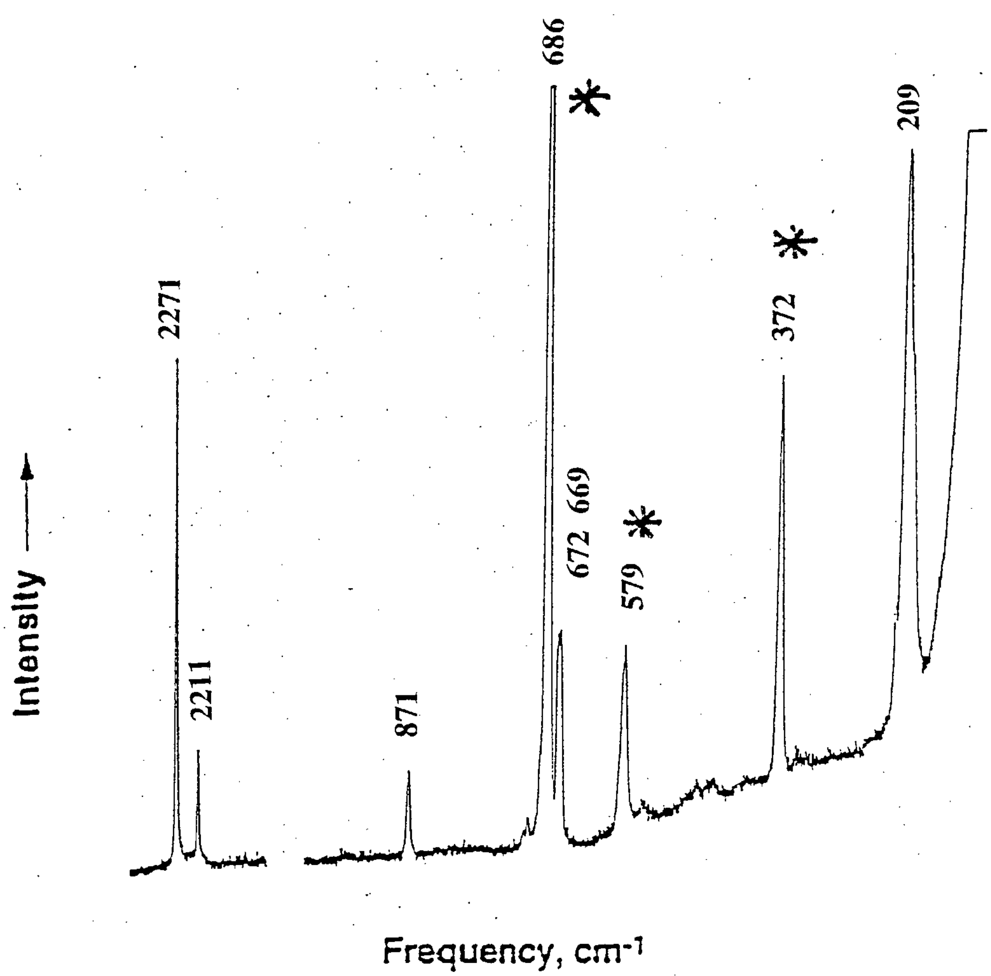
PHOTOGRAPH OF N_5AsF_6 IN QUARTZ TUBE

OPTIMIZED GEOMETRIES FOR N_5^+ CCSD(T) (B3LYP) VALUES



$[^{14}N-^{14}N-^{14}N-^{14}N-^{14}N]^+ AsF_6^-$

LOW-TEMPERATURE RAMAN SPECTRUM



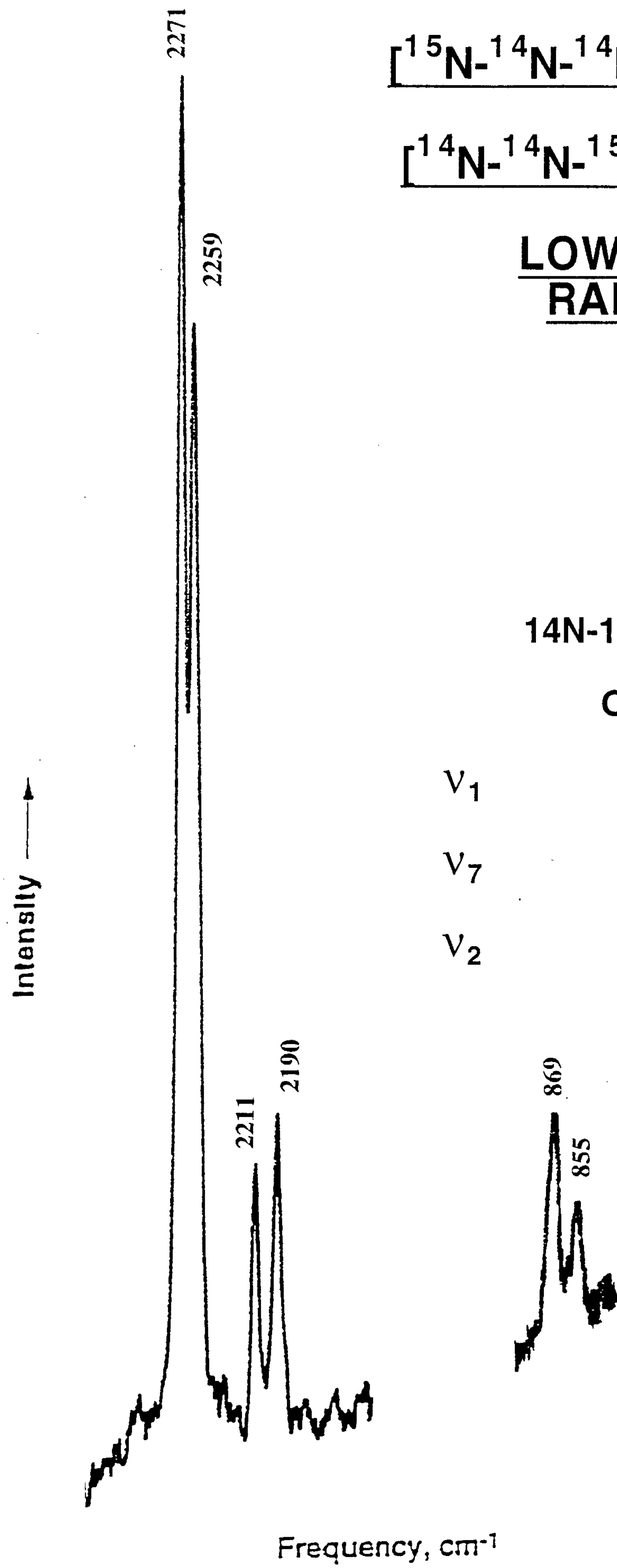
* = AsF_6^-

N_5^+	OBSD (cm^{-1})	CCSD(T) (cm^{-1})	B3LYP (cm^{-1})
ν_1 (A1)	2271	2229	2336
ν_7 (B2)	2211	2175	2282
ν_2 (A1)	871	818	850
ν_4 (A1)	209	181	193

$[^{15}N-^{14}N-^{14}N-^{14}N-^{14}N]^+ AsF_6^-$

$[^{14}N-^{14}N-^{15}N-^{14}N-^{14}N]^+ AsF_6^-$

LOW-TEMPERATURE RAMAN SPECTRUM

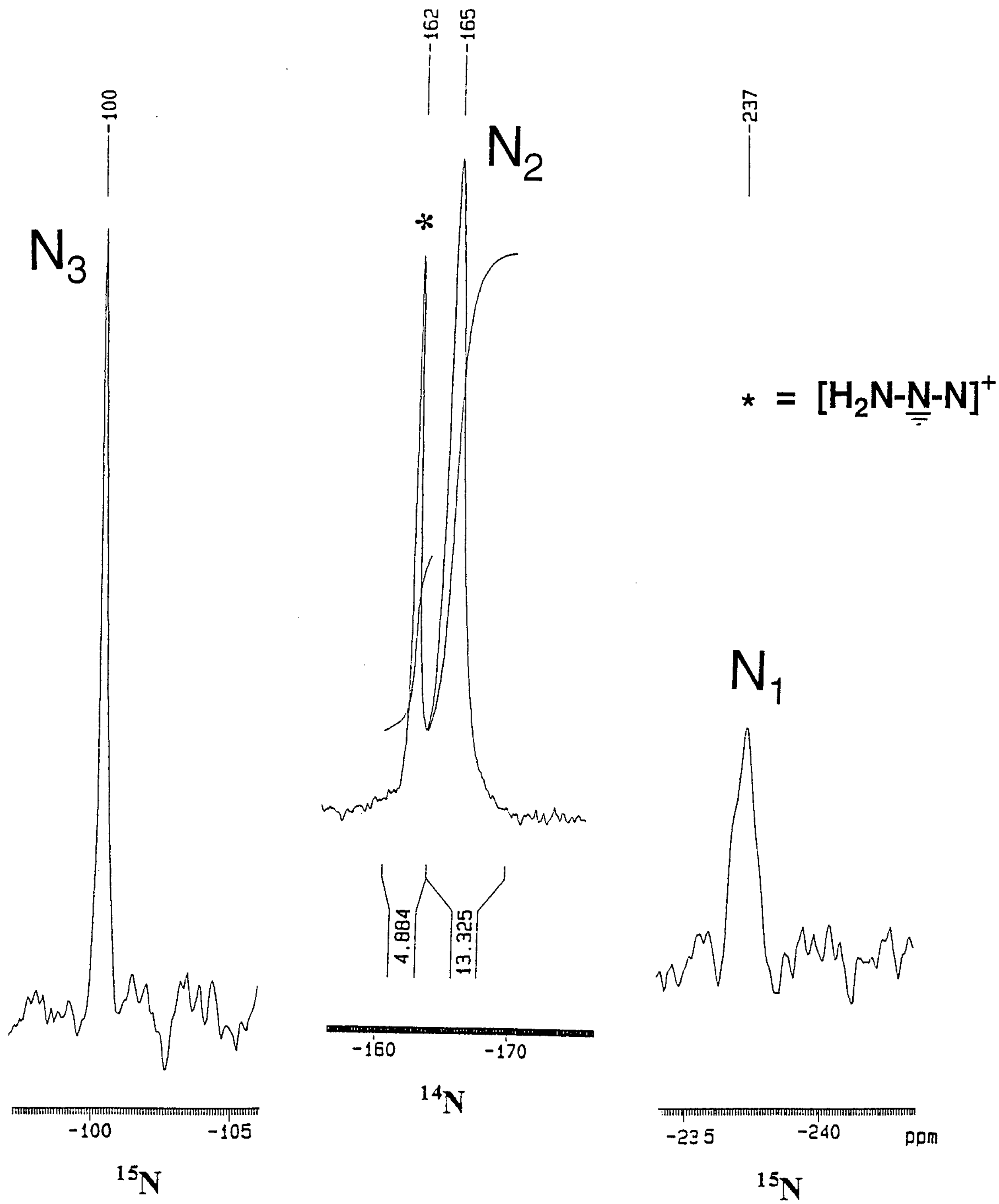


14N-15N SHIFTS (cm^{-1})

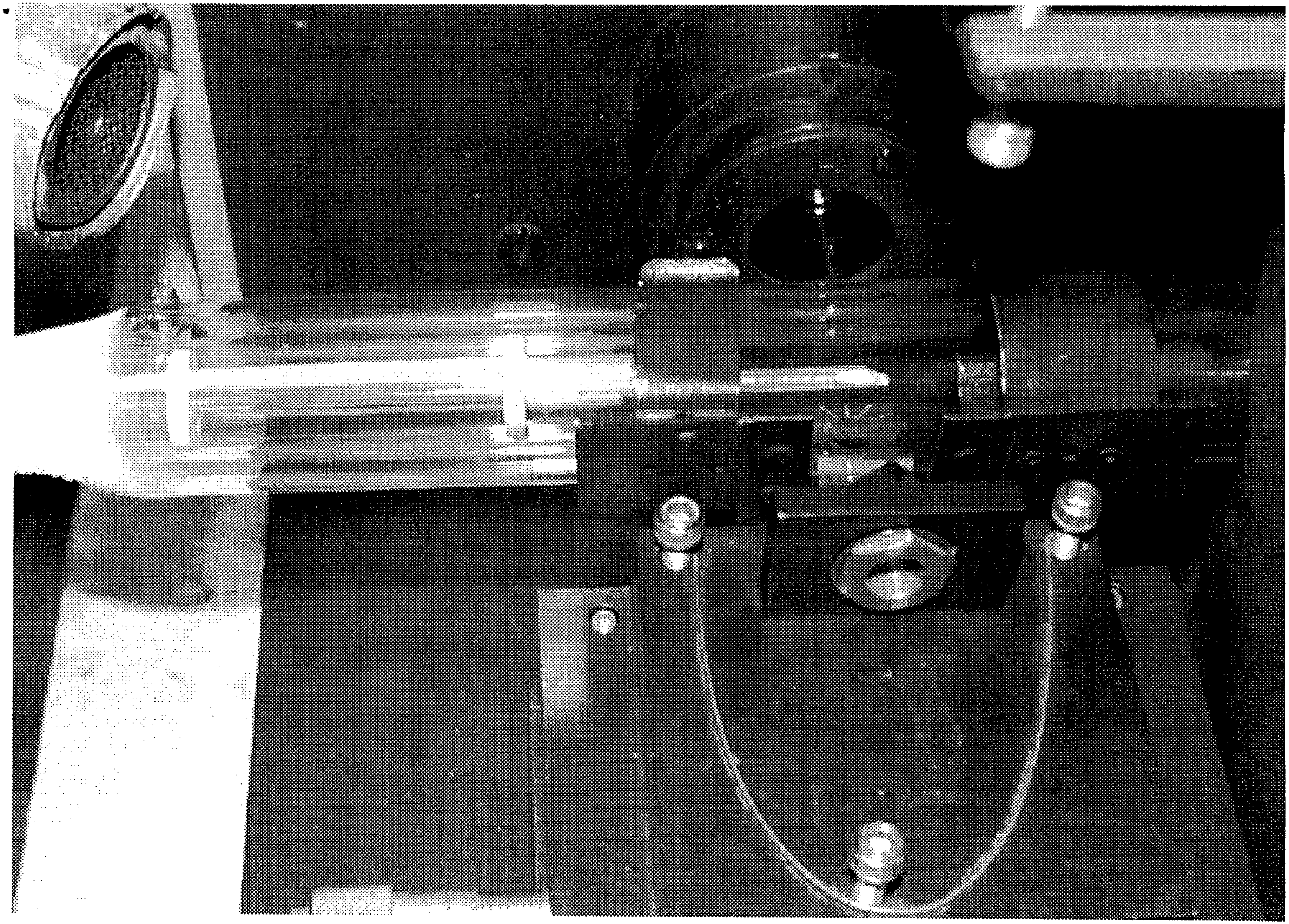
	OBSD	CALCD
ν_1	12	11.8
ν_7	21	21.4
ν_2	14	14.1

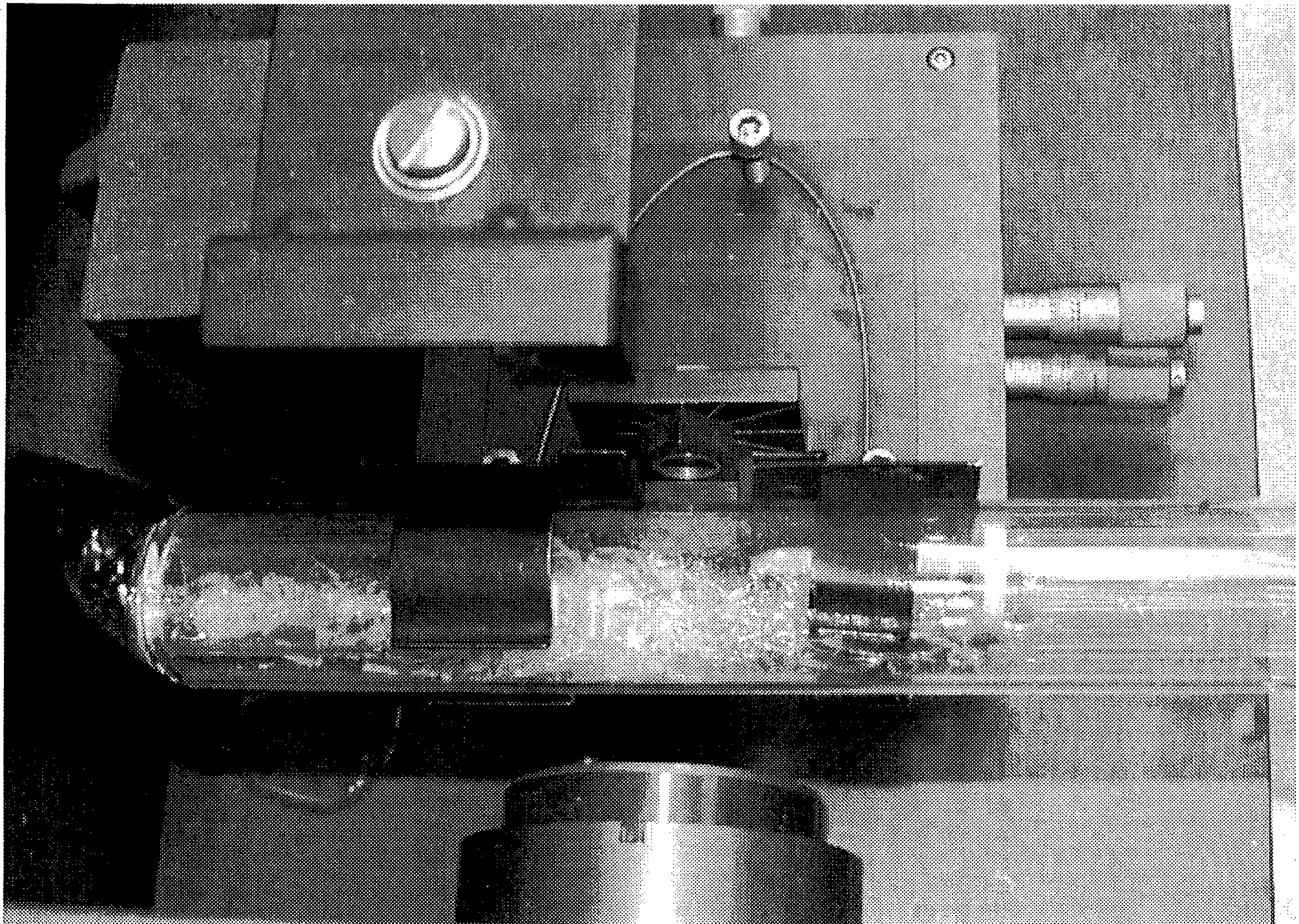
NITROGEN NMR SPECTRA OF

$[^{15}N\text{-}^{14}N\text{-}^{14}N\text{-}^{14}N\text{-}^{14}N]^+$ AND $[^{14}N\text{-}^{14}N\text{-}^{15}N\text{-}^{14}N\text{-}^{14}N]^+$



NMR SHIFTS (ppm)	OBSD	CALCD
N_1	-237.3	-235
N_2	-165.3	-166
N_3	-100.4	-95





WORK IN PROGRESS

- SYNTHESIS OF $N_5^+SbF_6^-$
- SENSITIVITY AND SAFETY DATA
- COMBINATION OF N_5^+ WITH POLYNITROGEN ANIONS TO PREPARE FIRST ALLOTROPE OF N_2
- SYNTHESIS OF XeN_3^+

SUMMARY

- A QUANTITATIVE SCALE FOR THE STRENGTH OF LEWIS ACIDS WAS DEVELOPED

- $N_5^+AsF_6^-$, THE ONLY HOMOLEPTIC POLYNITROGEN COMPOUND BESIDES N_2 AND N_3^- WHICH CAN BE MADE IN BULK, WAS PREPARED FROM $N_2F^+AsF_6^-$ AND HN_3 AND WAS CHARACTERIZED

- N_5^+ HAS A V-SHAPED CHAIN STRUCTURE AND IS MARGINALLY STABLE AT ROOM TEMPERATURE

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